The preparation of silicate compositions by a gelling method

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Summary. A method for the preparation of chemically homogeneous powders by a weighing and gelling technique is described in detail. Stress is placed on the importance of the weight yield as an indication of the bulk chemical composition and on the chemical analysis of several portions to test the homogeneity. A list of recommended chemicals is included in an appendix.

MANY studies in experimental petrology and allied branches of geology depend on having starting compositions from which small amounts can be taken and used in experiments. The essential properties of such starting materials are homogeneity and accurately known chemical composition. J. F. Schairer of the Geophysical Laboratory is well known for his excellent ground-glass starting materials, these have been used and tested by many people and have been found to fill these two requirements admirably. These glasses are homogeneous even when analysed on an electron microprobe (J. V. Smith, personal communication). However, the preparation of such glasses may be tedious and in some cases may require as many as ten fusions. This method is not recommended for the preparation of compositions having volatile constituents (e.g. Na, K) as these are preferentially lost during the numerous high-temperature fusions (Schairer and Bowen, 1955, 1956).

The co-precipitated gel method of preparing starting compositions has been used for at least ten years (Roy, 1956; Hamilton and MacKenzie, 1960; Luth and Ingamells, 1965). This method depends on one or more of the constituents forming a gel structure, the remaining non-gel-forming constituents presumably being held within the framework of the gel. The product of drying and then firing the gel at temperatures below 1000° C is a fine-grained powder that shows no birefringent material under the petrographic microscope and gives no X-ray diffrac-

tion pattern. This dried, decomposed, and fired material will in future be referred to as a 'gel'.

A 'gel' when used in hydrothermal heating experiments is very reactive and quickly produces a crystalline assemblage, but not necessarily the one having the lowest free energy. In certain experiments, therefore, a ground glass starting material, being a little less reactive, might be preferred. This may be made from the 'gel' by a single fusion followed by crushing. In more volatile systems it has been found possible to fuse a 'gel' in a closed platinum container and thus retain all the volatile constituents. In systems involving silicate crystal–liquid equilibria we have found no appreciable difference in the assemblages produced starting with 'gel' or ground glass.

Chemical analysis of 'gels'. There has been considerable speculation about the best way to test the homogeneity and chemical composition of 'gels'. Luth and Ingamells (1965) report analyses of 'gels' that were carried out to check the accuracy of their volumetric method for the addition of components.

If a 'gel' analysis agrees closely with the calculated composition (cf. analyses in Luth and Ingamells, 1965) than the 'gel' is presumably homogeneous and can be said to be *on* composition. However, analytical results can be equivocal and our main reservations concerning the meaning of an analysis are, first, that 'gels' are particularly hygroscopic and difficult to completely dehydrate (even above 1000° C); it is, therefore, difficult to be sure of the absolute weight (water free) of a portion of 'gel' taken for analysis. And secondly, if the replicate analyses of a 'gel' for a particular element showed good precision but were consistently high or low as compared with the calculated figure this could be attributed to consistent error on the part of the analyst or analytical method, or, if the results are consistently low, to the 'gel' being hydrous; if the results are an accurate reflection of the bulk composition the 'gel' would be *off* composition.

We feel, therefore, that it is better to analyse 'gels' to test their homogeneity rather than to determine their absolute composition. The method of 'gel' preparation described below employs only weighings of pure chemicals and, neglecting any accidents, the bulk chemical compositions depends only on the accuracy of weighing and on the purity of the chemical compounds and reagents used in the preparation. We think that the weight yield of a 'gel' is a good indication of its reliability and we find that compositions made up and fired in the same platinum container give yields in the range 100·0–100·5 %. The small extra weight

is probably due to absorbed water. Thus we know accurately what we have added and if the 'gels' are shown to be homogeneous then they must be *on* composition.

The homogeneity of some 'gels' has been tested by analysing several portions using added radioactive tracers, and the results are discussed below.

Starting materials used. The choice of chemicals used in preparing a 'gel' is critical. Ideally only the highest purity chemicals available should be used but if a large number of 'gels' are to be made a compromise between expense and purity has to be made. For 'gels' in which purity is of the utmost importance (e.g. for those to be used as standards in microprobe and X-ray fluorescence analysis or in trace-element distribution studies) Johnson–Matthey Grade I high-purity chemicals are recommended; the purity of these is normally near to 99·999 %. For less exacting work Johnson–Matthey Grade II chemicals are advised, these are normally near to 99·99 % purity and are much less expensive. ANALAR grade chemicals may also be satisfactory. The appendix contains a list of chemicals that have been used and found to be satisfactory. Two sources of SiO_2 are available; one is tetraethyl orthosilicate (T.E.O.S.) and the other is an ammonia-stabilized colloidal solution (Ludox). Either are satisfactory but we prefer T.E.O.S. for three reasons:

Although it is volatile it loses SiO_2 stoichiometrically and thus loss before gelling can be allowed for in the initial weighing; if allowed to stand for a long time it will absorb water and hydrolyse but experiments have shown that T.E.O.S. weighed and allowed to stand for three hours before being reweighed and gelled gives an identical yield to that gelled directly.

Ludox contains some Na_2O and this amount varies considerably from batch to batch (see appendix); thus in soda-bearing systems a correction should be made for the Na_2O contributed by the Ludox and in soda-free systems Ludox should not be used as a source of SiO_2.

Evaporation of water from Ludox will concentrate the SiO_2 and Na_2O and it must be kept in a tightly stoppered bottle; yields of SiO_2 and Na_2O should therefore be determined frequently.

Method of 'gel' preparation. Each dried chemical powder is weighed to $\pm 0 \cdot 2$ mg and transferred to a P.T.F.E. (Teflon) beaker. When all the required powders are in the beaker enough nitric acid is introduced to convert all the elements to nitrates. For compositions containing Al the beaker is immersed in the water bath and left for a few hours as the

finely divided Al metal powder used dissolves very slowly even in hot nitric acid. The solution is then evaporated to dryness (or nearly so) to remove excess nitric acid and the residue redissolved in a small volume of water. The required weight of T.E.O.S. is washed into the beaker with ethyl alcohol, enough alcohol being added to render the T.E.O.S and nitrate solution miscible (approximately one part of alcohol to one part of T.E.O.S. plus nitrate solution). The resultant solution is homogeneous and contains all the elements in the requisite proportions. Ammonium hydroxide (D 0·88) is now added to precipitate the silica, the solution being stirred continuously, and the gelling is normally completed in less than a minute. The product should be a stiff porridge-like gel with no supernatant solution. (If Ludox is used as a source of SiO_2 it is weighed and washed into the beaker with water; the solution can now either be allowed to gel slowly, in hours or days depending on the bulk composition, or can be instantaneously gelled by addition of ammonia.) The gel is allowed to stand overnight at room temperature to ensure complete precipitation before drying on a water bath and then in an oven at 110° C. The completely dried 'gel' is now ground in an agate mortar and then transferred to a crucible. The nitrates are decomposed slowly over a bunsen flame, and then the 'gel' is fired in a furnace at about 800° C. At this stage the 'gel' is ready for use, but if any sintering has occurred it should be ground once again.

Iron-bearing gels should not be evaporated to dryness before addition of T.E.O.S. otherwise the ferric nitrate decomposes and residual oxide is difficult to redissolve. If one of the starting chemicals is very hygroscopic (e.g. Cs_2CO_3) a portion should be quickly and accurately weighed and then the weights of the other components recalculated to give the required composition.

The use of P.T.F.E. beakers is recommended as nearly 100 % of the dried 'gel' can be removed relatively easily and they can be cleaned thoroughly in hydrofluoric acid before re-use. The firing of the 'gels' is best done in platinum crucibles but 'gels' containing transition elements should be fired in alundum or other suitable ceramic crucibles.

Homogeneity of 'gels'. Most compositions used in this department are aluminosilicates of the alkali and alkaline earth metals. The body of these 'gels' is made up of Si and O (and presumably Al) and other elements are held in the 'gel' framework. It is assumed that if the 'gels' are found to have the alkali elements distributed homogeneously there is no reason to suppose other elements (e.g. Ca, Mg, Fe) would be unevenly distributed.

Three 'gels' of composition 50 $NaAlSi_2O_6$:50 $KAlSi_2O_6$ (wt. %) and one of composition 50 $KAlSi_2O_6$:50 $RbAlSi_2O_6$ have been prepared, and their homogeneity determined. High purity carbonates of Na, K, and Rb were irradiated and added as tracers. One of the K–Na 'gels' and the K–Rb 'gel' were prepared and fired in platinum basins and yields

TABLE I. Test of homogeneity of alkali aluminosilicate 'gels'

'Gel'	Number of portions counted	Counts per sec per mg	Standard deviation of measurements (s)	Relative deviation (C) %
Counts for total $(Na+K)$ β activity				
1	8*	0·727, 0·734, 0·718, 0·721, 0·698, 0·730, 0·712, 0·722	0·011	1·5
2 $\{$ a	4	5·62, 5·74, 5·60, 5·91	0·14	2·5
$\quad$ b	3	3·46, 3·48, 3·46	0·012	0·35
3	3	2·44, 2·47, 2·38	0·046	1·9
Counts for K β activity				
1	3	1·13, 1·13, 1·14	0·006	0·53
2	3	0·233, 0·226, 0·234	0·004	1·9
3	3	0·216, 0·218, 0·216	0·0012	0·56
Counts for Rb β activity				
4	3	1·56, 1·54, 1·59	0·025	1·6

* Individual portions vary from 30·4 to 329·4 mg.

1. 50 $NaAlSi_2O_6$: 50 $KAlSi_2O_6$ (T.E.O.S. used) ⎫ Active K and
2. 50 $NaAlSi_2O_6$: 50 $KAlSi_2O_6$ (Ludox used) ⎬ Na added.
3. 50 $NaAlSi_2O_6$: 50 $KAlSi_2O_6$ (Ludox used) ⎭
4. 50 $KAlSi_2O_6$: 50 $RbAlSi_2O_6$ (Ludox used)   Active Rb added.

Weight yield of 1 was 100·3 %; 4 was 100·03 %.

accurately determined (table I). The other two were prepared in P.T.F.E. beakers and after being evaporated to dryness were carefully transferred to platinum crucibles without any grinding or mixing as transferal of material from beaker to crucible cannot be completely quantitative and it is, therefore, important to know the homogeneity of the 'gel' at this stage. The sample portions were weighed onto Al trays and counted for total $(Na+K)$ β-activity and then for K β-activity (Winchester, 1961). Because of the short half-lives of Na^{24} (15·0 h) and K^{42} (12·4 h) and low count rates the statistical accuracy of the counting is in the range ± 0.5–2.0 %. The material mounted on the trays varied in size from a very fine powder to lumps up to 3 mm

diameter. The results are given in table I, and an indication of the homogeneity of each gel is given by the relative deviations of the count rates for different portions of the same 'gel'.

Sample 1 was found to have similar count rates per mg for samples varying from 30·4 to 329·4 mg: 30 mg is the usual minimum weight of 'gel' taken in our experimental investigations. Most of the variation in activity is thought to be due to the lumpiness of the material introducing counting geometry and self-absorption errors. This was tested for 'gel' 2 by counting the total activity for lumpy samples and then for finely powdered samples; the comparative relative deviations of the count rates are 2·5 and 0·35 % respectively.

The homogeneity of the 'gels' before grinding and mixing, as estimated from the relative deviations given in table I, is therefore seen to be of the same order as the statistical accuracy of the counting. The actual homogeneity may, in fact, be better than this. It is, therefore, assumed that after thorough grinding and mixing the 'gel' will be completely homogeneous.

Samples of 'gels' 1, 2, and 3 were crushed fine, weighed, and mounted on Al trays and counted against a standard to determine the yield of activity relative to that added. 'Gels' 1, 2, and 3 for total ($Na+K$) counts gave yields of 99, 96, and 102 % respectively. Counts for K alone gave yields of 100·5, 98, and 100·5 %. The yields of activity are very close to 100 % indicating the 'gels' are on composition as far as Na and K are concerned. The agreement for the three 'gels' is very good bearing in mind that the count rates are low and that it is difficult to compare one 'gel' with another (or to standards) as the degree of hydration will vary slightly.

Conclusions. The results discussed above show that within the limits of analytical error 'gels' made in the described manner are homogeneous even before they are ground and mixed. As the weights of the various components added are known accurately and the weight-yields of gels are very close to 100 % then they must also be *on* composition. This was substantiated by comparing the activity of the 'gels' with standards in order to determine the percentage yield of activity compared with that added.

References

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Appendix. Recommended starting chemicals and their sources

Si: (a) Tetraethyl orthosilicate (T.E.O.S.). Monsanto Chemicals. Yields of SiO_2 determined on various batches are constant at approximately 99·7 %. The low yield may be due to the presence of a small amount of ethyl alcohol. HF/H_2SO_4 evaporation of SiO_2 leaves a residue of less than 0·03 wt. %. The precipitated SiO_2 was analysed for Na and K by radioactivation analysis but these elements were not detected. (b) Ludox. Du Pont Chemicals. One batch analysed by C. M. B. H. gave 0·3088 gm SiO_2 per gm Ludox; residue after HF/H_2SO_4 evaporation was 0·0010 gm per gm solution. Analysis for Na_2O gave 0·34 mg Na_2O per gm Ludox. A batch analysed for D. L. H. by C. O. Ingamells for SiO_2, R_2O_3, and Na_2O gave 0·3076 gm, 0·00075 gm, and 4·36 mg per gm Ludox respectively. Another batch analysed by Ingamells yielded 3·05 mg Na_2O/gm Ludox.

Al: (a) Al metal 99·99 % pure. British Aluminium Co. Ltd., London, S.W. 1. The yield of Al_2O_3 was 99·9 % Al_2O_3; it is therefore assumed that 0·1 % Al_2O_3 was present initially. (b) Al metal 99·999 % pure. Halewood Chemicals Ltd., Horton Rd., Stanwell Moor, Staines, Middlesex. It is important that the Al metal used should be in a very finely divided state otherwise difficulty will be experienced in completely dissolving it, even in hot nitric acid.

Fe: British Chemical Standards metallic Fe, 99·5 % pure. Bureau of Analysed Samples, Newton Hill, Middlesbrough, Yorks.

Mg: (a) High Purity, Grade I, Mg Crystals. Johnson-Matthey & Co., Ltd., Hatton Garden, London, W.C. 1. (b) Metallic Mg 99·95 % pure (including 0·2 % MgO) Magnesium Elektron Ltd., Clifton Junction, Nr. Manchester.

Na: (a) High Purity, Grades I and II, Na_2CO_3. Johnson-Matthey. (b) ANALAR Na_2CO_3.

K: (a) High Purity, Grade I, K_2CO_3. Johnson-Matthey. (b) ANALAR K_2CO_3.

Rb,Cs: High Purity, Grade II, carbonates. Johnson-Matthey.

Minor and trace amounts of transition elements have been added as ammonium metavanadate, metallic Co and Mn, and oxides of Cu and Ni, all Johnson-Matthey Grade I High Purity chemicals.